Thermodynamics and information theory: entropy of quantum ensembles

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ABSTRACT. Quantum ensembles are classified according to information which may be available in addition to the knowledge of density operator ρ. Moreover, it is proved that if $\$(\rho) = -k\ \mathrm{Tr}(\rho \ln \rho)$ is $1/N$ times the entropy of any after-measurement ensemble with N elements and described by ρ, then the highest entropy principle would be violated.

RÉSUMÉ. Les ensembles quantiques sont classés suivant les informations disponibles en sus de l'opérateur densité ρ. En outre, on démontre que si $\$(\rho) = -k\ Tr(\rho \ln \rho)$ est $1/N$ fois l'entropie de chaque ensemble après une mesure avec N éléments décrits par ρ, alors le principe de l'entropie maximale serait violé.

I. Introduction

In quantum statistical mechanics, the entropy of a macroscopic system A whose thermodynamic state is represented by a density operator ρ on the Hilbert space $\mathcal{H}_A$ of A is given by

$$\$(\rho) = -k\ \mathrm{Tr}(\rho \ln \rho), \tag{1.1}$$

where k is Boltzmann constant.

A stronger interpretation of functional (1.1) is proposed by von Neumann in his celebrated book [1]. The author states that functional (1.1) represents $1/N$ times the entropy of any ensemble $\mathcal{E}$ described by density operator ρ and composed of N macroscopic or microscopic systems. Functional \$ is defined on the set of density operators $\{\rho\}$ on the Hilbert

space $\mathcal{H}_A$ of any quantum system A. In particular, (1.1) is considered as $1/N$ times the entropy of any after-measurement ensemble with N elements. This statement appears explicitly in Ref.[1], in a proof of the irreversibility of an ideal measurement of any observable Ω which does not commute with ρ,

$$\rho \to \hat{\rho} = \sum_{\alpha} P_\alpha \rho P_\alpha, \tag{1.2}$$

where $\{P_\alpha\}$ are the projectors on the eigenspaces $\{\mathcal{H}_A^\alpha\}$ of Ω. The purposes of this paper are the following.

a) To show that non-pure quantum ensembles can be classified according to information which is not given by density operator ρ. For instance, this information can concern the ordering of the ensemble, i.e. the correspondence between a prescribed element of the ensemble and a pure quantum state.

b) To prove that the interpretation of functional (1.1) as $1/N$ times the entropy of any after-measurement ensemble with N elements violates the highest entropy principle.

The paper is organized as follows. In section II, quantum ensembles are classified according to information which may be available in addition to the knowledge of density operator ρ. Then, a missing information functional is defined. In section III, von Neumann's treatment of functional (1.1) is analysed and restated in order to prove that, for a mixture of orthogonal states described by a density operator ρ, $\$(\rho)$ equals $1/N$ times the entropy of an N-particle mixture of ideal gases associated with the ensemble. Finally, in section IV purpose b) is accomplished.

II. Missing information

In this section, quantum ensembles are classified according to information which may be available in addition to the knowledge of density operator ρ. Then, a missing information functional is defined.

An ensemble $\mathcal{E}$ of identical systems A is a set of replicas of A, which either do not coexist or coexist but are sufficiently separated in space, so that they are both distinguishable and non-interacting. For instance, in Ref.[1], chapter V, section 2, it is stated that "We are dealing with ... an ensemble of very many (identical) mechanical systems ... each of which is entirely separated from the others, and does not interact with any of them. As a consequence ..., it is evident that ordinary statistics shall be used, and that the Bose-Einstein and Fermi-Dirac statistics, which ...

are applicable to certain ensembles of indistinguishable ... particles ..., do not enter into the problem".

Given an ensemble $\mathcal{E}$ of identical systems A, the statistics of measurement outcomes of all observables of A at any instant t are completely determined by a density operator ρ on the Hilbert space $\mathcal{H}_A$ of system A. However, if $\rho \neq \rho^2$, information on $\mathcal{E}$ not given by ρ can exist. In fact, if $\rho \neq \rho^2$, although there is a unique orthonormal basis $\{|\psi_n\rangle\}$ which diagonalizes ρ, there exist infinite different sets of non-orthogonal projectors $\{|\varphi_n\rangle\langle\varphi_n|\}$ such that $\rho = \sum_n c_n|\varphi_n\rangle\langle\varphi_n|$, as it is proved in Ref.[2]. Therefore, one cannot associate to a density operator $\rho \neq \rho^2$ a unique set of pure quantum states. On account of this circumstance, the information that a non-pure quantum ensemble $\mathcal{E}$ is the union of pure subensembles, each in a pure state $|\varphi_n\rangle$, cannot be obtained by the knowledge of density operator ρ. Moreover, if this information is available, one can either know or ignore which elements of $\mathcal{E}$ are in a prescribed state $|\varphi_n\rangle$.

An ensemble $\mathcal{E}$ of identical systems A will be called an *ordered ensemble* if the state of each replica of A is known. For example, an ensemble $\mathcal{E}$ in a known pure state $|\varphi\rangle$ is ordered. Moreover, any after-measurement ensemble obtained by a complete ideal measurement process is ordered even if $\rho \neq \rho^2$. In fact, the members of an ensemble are distinguishable by definition, and a complete ideal measurement assigns to each of them a set of real numbers (eigenvalues of the complete set of measured observables) which determines a unique quantum state. Therefore, at the end of the measurement the state of each replica of A is known.

If an ensemble $\mathcal{E}$ is not ordered, it will be called a *non-ordered ensemble*. Even if $\mathcal{E}$ is non-ordered, it is possible to have information on $\mathcal{E}$ not given by ρ. For instance, an information on $\mathcal{E}$ not given by ρ can be the following: a fraction c_1 of the elements of $\mathcal{E}$ is in the pure state $|\varphi_1\rangle$, a fraction c_2 is in the pure state $|\varphi_2\rangle, \ldots$. If $\mathcal{E}$ is non-ordered and this information is available, $\mathcal{E}$ will be called a *mixture of specified states* and will be denoted by $\mathcal{E}\{c_n, |\varphi_n\rangle\}$. This information is not given by ρ because, as it has been pointed out above, any density operator $\rho \neq \rho^2$ can be written as a linear combination of projectors, $\rho = \sum_n c_n|\varphi_n\rangle\langle\varphi_n|$, by infinite different choices of the linear independent system of state vectors $\{|\varphi_n\rangle\}$ [2]. However, one can conceive physical situations in which this information is available. Let us consider, for example, an initially ordered ensemble $\mathcal{E}$ and suppose that any other

information has been lost except the fractions $\{c_n\}$ of members of $\mathcal{E}$ which are in states $\{|\varphi_n\rangle\}$.

Let us consider a mixture of specified states, $\mathcal{E}\{c_n, |\varphi_n\rangle\}$. The following cases are possible:

a) the set of states $\{|\varphi_n\rangle\}$ is orthogonal;

b) the set of states $\{|\varphi_n\rangle\}$ is not orthogonal.

In case a), $\mathcal{E}\{c_n, |\varphi_n\rangle\}$ will be called a *mixture of orthogonal states*; in case b), $\mathcal{E}\{c_n, |\varphi_n\rangle\}$ will be called a *mixture of non-orthogonal states.*

A mixture of non-orthogonal states can be obtained experimentally. For instance, let $\mathcal{E}$ be an ensemble of spin-1/2 particles. First, a measurement of the spin component along direction $\overline{z}$ is performed on $\mathcal{E}$ by a Stern-Gerlach apparatus. Thus, $\mathcal{E}$ is partitioned into two pure subensembles: $\mathcal{E}_z^+$ and $\mathcal{E}_z^-$. Then, a measurement of the spin component along a direction $\overline{v}$ not orthogonal to $\overline{z}$ is performed on $\mathcal{E}_z^+$. Thus, $\mathcal{E}_z^+$ is partitioned into two pure subensembles : $\mathcal{E}_v^+$ and $\mathcal{E}_v^-$. The result is an ordered ensemble $\hat{\mathcal{E}}$ given by the union of $\mathcal{E}_z^-$, $\mathcal{E}_v^+$ and $\mathcal{E}_v^-$. If any other information is lost except the fractions of members of $\hat{\mathcal{E}}$ which are in states $|z^-\rangle$, $|v^+\rangle$ and $|v^-\rangle$, a mixture of non-orthogonal states is obtained.

An important physical difference exists between cases a) and b). In fact, in case a) there exists an ideal measurement which allows us to transform $\mathcal{E}\{c_n, |\varphi_n\rangle\}$ into an ordered ensemble $\mathcal{E}'$ in which a fraction c_n of member systems is in state $|\varphi_n\rangle$, for every n. This measurement allows us to recover the information on $\mathcal{E}'$ which has been lost. On the contrary, in case b) no ideal measurement exists which allows us to transform $\mathcal{E}\{c_n, |\varphi_n\rangle\}$ into an ordered ensemble $\mathcal{E}'$ in which a fraction c_n of member systems is in state $|\varphi_n\rangle$, for every n. Therefore, it is impossible to recover the information on $\mathcal{E}'$ which has been lost. These statements are proved by the following theorems.

Theorem 1. If $\mathcal{E}\{c_n, |\varphi_n\rangle\}$ is a mixture of orthogonal states, there exists an observable Ω such that an ideal measurement of Ω transforms $\mathcal{E}\{c_n, |\varphi_n\rangle\}$ into an ordered ensemble $\mathcal{E}'$ in which a fraction c_n of member systems is in state $|\varphi_n\rangle$, for every n.

Proof. Let us consider the following self-adjoint operator on $\mathcal{H}_A$:

$$\Omega = \sum_n n|\varphi_n\rangle\langle\varphi_n|. \tag{2.1}$$

An ideal measurement of Ω associates number n with each member of $\mathcal{E}\{c_n, |\varphi_n\rangle\}$ in state $|\varphi_n\rangle$, so that different numbers are associated with members in different states. Therefore, the after-measurement ensemble is the ordered ensemble $\mathcal{E}'$ described in the thesis.

Theorem 2. If $\mathcal{E}\{c_n, |\varphi_n\rangle\}$ is a mixture of non-orthogonal states, no ideal measurement can transform $\mathcal{E}\{c_n, |\varphi_n\rangle\}$ into an ordered ensemble $\mathcal{E}'$ in which a fraction c_n of member systems is in state $|\varphi_n\rangle$, for every n.

Proof. In order to transform $\mathcal{E}\{c_n, |\varphi_n\rangle\}$ into $\mathcal{E}'$, a complete ideal measurement should yield the same list of measurement outcomes $l_n = (a_n, b_n, \ldots)$ for all member systems of $\mathcal{E}\{c_n, |\varphi_n\rangle\}$ in state $|\varphi_n\rangle$, such that $l_n \neq l_m$ if $n \neq m$. If $l_n \neq l_m$ at least one measurement outcome differs in the two lists, say $a_n \neq a_m$. Therefore, the linear self-adjoint operator A with eigenvalues $\{a_n\}$ should have non-orthogonal eigenvectors corresponding to different eigenvalues, in contrast with a well known theorem of linear algebra [3].

Quantum ensembles have been thus classified into ordered and non-ordered ensembles. The latter can be:

i) ensembles about which no other information is available except the knowledge of density operator $\rho \neq \rho^2$;

ii) mixtures of orthogonal states;

iii) mixtures of non-orthogonal states.

The distinction between ordered and non-ordered ensembles is qualitatively different from that between i), ii) and iii). Indeed, for an ordered ensemble with $\rho \neq \rho^2$ the information not given by ρ can be checked experimentally. On the contrary, for a non-ordered ensemble the information not given by ρ cannot be checked experimentally. This information can be owned by an observer, but cannot be verified by another observer. In fact, for any complete ideal measurement, both the statistics of measurement outcomes and the ordered ensemble obtained after measurement are completely determined by ρ and by the set of measured observables.

In information theory [4] the following function is defined. If we know that one of W equiprobable events has happened, but we ignore which one, then some information is missing and its amount is given by:

$$I(W) = \alpha \ln W, \tag{2.2}$$

where α is an arbitrarily chosen real positive constant. $I(W)$ is called *missing information* about the event. The concept of missing information can be applied to a mixture of orthogonal states $\mathcal{E}\{c_n, |\varphi_n\rangle\}$, as follows.

Let us consider a mixture of orthogonal states $\mathcal{E}\{c_n, |\varphi_n\rangle\}$, described by density operator $\rho = \sum_{n=1}^{q} c_n |\varphi_n\rangle\langle\varphi_n|$. $\mathcal{E}\{c_n, |\varphi_n\rangle\}$ is an ensemble of $N \gg 1$ identically prepared replicas of system A, such that: $c_1 N$ replicas of A are in state $|\varphi_1\rangle$, $c_2 N$ replicas of A are in state $|\varphi_2\rangle, \ldots, c_q N$ replicas of A are in state $|\varphi_q\rangle$. Compatibly with the available information, the number of possible correspondences between the N replicas of A and the q states $|\varphi_1\rangle, \ldots, |\varphi_q\rangle$, is given by:

$$W_{\mathcal{E}} = \frac{N!}{\Pi_{n=1}^{q}(Nc_n)!}. \tag{2.3}$$

As a consequence of eqs.(2.2) and (2.3), the missing information $I(W_{\mathcal{E}})$ about the ensemble $\mathcal{E}\{c_n, |\varphi_n\rangle\}$ is given by :

$$\begin{aligned} I(W_{\mathcal{E}}) &= \alpha\Big[\ln N! - \sum_{n=1}^{q} \ln(Nc_n)!\Big] \\ &= \alpha\Big[N\ln N - N - \sum_{n=1}^{q} Nc_n \ln(Nc_n) + \sum_{n=1}^{q} Nc_n\Big] - g(N), \end{aligned} \tag{2.4}$$

where Stirling's formula [5] has been used. Function $g(N)$ is such that:

$$\lim_{N\to\infty} \frac{g(N)}{\ln N} = \frac{q-1}{2},$$

and, as a consequence, $g(N)/N$ vanishes for $N \to \infty$.

Eq. (2.4) yields :

$$\begin{aligned} I(W_{\mathcal{E}}) &= \alpha\Big[(1 - \sum_{n=1}^{q} c_n)(N\ln N - N) - N(\sum_{n=1}^{q} c_n \ln c_n)\Big] - g(N) \\ &= -\alpha N(\sum_{n=1}^{q} c_n \ln c_n) - g(N) = -\alpha N \ \mathrm{Tr}(\rho\ln\rho) - g(N), \end{aligned} \tag{2.5}$$

where the normalization condition $\sum_{n=1}^{q} c_n = \ \mathrm{Tr}\rho = 1$ has been used.

Definition of Missing Information. Let us define *missing information on a mixture of orthogonal states* $\mathcal{E}\{c_n, |\varphi_n\rangle\}$ the quantity:

$$I(\mathcal{E}\{c_n, |\varphi_n\rangle\}) = \lim_{N\to\infty} \frac{I(W_\mathcal{E})}{N}. \tag{2.6}$$

On account of eqs.(2.5) and (2.6):

$$I(\mathcal{E}\{c_n, |\varphi_n\rangle\}) = -\alpha \operatorname{Tr}(\rho \ln \rho). \tag{2.7}$$

The real constant α, which appears in eq.(2.7), can be arbitrarily chosen and determines the physical dimensions of $I(\mathcal{E}\{c_n, |\varphi_n\rangle\})$.

If $\rho = \sum_n c_n |\varphi_n\rangle\langle\varphi_n|$ has infinite nonvanishing eigenvalues, the missing information on $\mathcal{E}\{c_n, |\varphi_n\rangle\}$ can be defined as follows. First, let us consider a density operator $\rho' = \sum_{n=1}^{q} c_n |\varphi_n\rangle\langle\varphi_n|$ and define functional I_q by eq.(2.6); then let us take the limit $q \to \infty$ of I_q. With this definition, eq.(2.7) still holds. If ρ has a continuous spectrum, the missing information on $\mathcal{E}\{c_n, |\varphi_n\rangle\}$ can be defined in a similar way.

The definition of missing information stated above for mixtures of orthogonal states can be extended to ordered ensembles. In this case, the state of each element of the ensemble $\mathcal{E}$ is known so that, compatibly with the available information, the number $W_\mathcal{E}$ of correspondences between the N replicas of A and the q states $|\varphi_1\rangle, \ldots, |\varphi_q\rangle$ is 1. Therefore, on account of eq.(2.2), the missing information on $\mathcal{E}$ is zero.

III. Mixing entropy

In this section, von Neumann's treatment of functional $\$(\rho) = -k \operatorname{Tr}(\rho \ln \rho)$ is analysed and restated in order to prove that, for a mixture of orthogonal states described by density operator ρ, $\$(\rho)$ represents $1/N$ times the entropy of an N-particle multicomponent ideal gas associated with the ensemble, if an appropriate choice of the entropy constants of the pure components is made.

In Ref.[1] von Neumann presents a long treatment in order to prove that $\$(\rho) = -k \operatorname{Tr}(\rho \ln \rho)$ is $1/N$ times the entropy of any ensemble $\mathcal{E}$ composed of N elements and described by density operator ρ. However, the treatment proves only that $\$(\rho)$ is $1/N$ times the entropy of an appropriate N-particle mixture $\mathcal{S}$ of ideal gases in the stable equilibrium state with temperature T and volume-per-particle $v = V/N$, if the entropy of any monocomponent ideal gas in the stable equilibrium state with temperature T and volume-per-particle v is taken as zero.

In fact, the author associates with the given ensemble $\mathcal{E}$ a supersystem $\mathcal{S}$, in a stable equilibrium state with temperature T, obtained as follows. "Each system ... is confined in a box ... whose walls are impenetrable to all transmission effects ... each box must have a very large mass ... We then enclose these boxes into a very large box $\overline{K}$ ... we now bring $\overline{K}$ into contact with a very large heat reservoir of temperature T ... We can then say: the gas has taken on the temperature T". Supersystem $\mathcal{S}$ cannot be identified with the given ensemble $\mathcal{E}$, in its original quantum mechanical state, for the following reasons.

a) The elementary constituents of $\mathcal{S}$ are boxes with a very large mass, and not the elements of $\mathcal{E}$ (i.e., the replicas of system A). The quantum mechanical state of the replica of A contained in each box is just a label which makes two elementary constituents of $\mathcal{S}$ different if they have different labels. Therefore, the dynamical state of each elementary constituent of $\mathcal{S}$ (i.e. a box) is completely independent of the quantum mechanical state of the replica of A contained therein. Moreover, the time evolution of each replica of A, determined by the hamiltonian of A, is completely independent of the time evolution of the gas of boxes $\mathcal{S}$, which interacts with the heat reservoir.

b) An ensemble is a collection of systems, which either do not exist simultaneously or exist simultaneously and are widely separated in space. In the first case, the ensemble cannot be considered as a system. In the second case, the ensemble can be considered as a system of distinguishable particles. This system cannot coincide with supersystem $\mathcal{S}$ considered in Ref.[1], because identical particles of $\mathcal{S}$ are indistinguishable, as it is proved in the following.

Let us suppose by absurd that identical particles of $\mathcal{S}$ are distinguishable, i.e., $\mathcal{S}$ is a classical statistical system. This hypothesis is incompatible with the treatment presented in Ref.[1], where it is proved that all supersystems $\mathcal{S}$ of identical boxes with the same temperature T and volume-per-particle v have the same entropy-per-particle $s = S/N$. In fact, classical statistical systems have the following behaviour. If two classical monocomponent ideal gases $\mathcal{A}$ and $\mathcal{B}$, with the same component and the same values of temperature T, volume-per-particle v, entropy-per-particle s, are mixed while $\mathcal{A} + \mathcal{B}$ is isolated, then $\mathcal{A} + \mathcal{B}$ reaches a final state with temperature T, volume-per-particle v and an entropy-per-particle $s' \neq s$ [6].

To summarize, if the author assumes that ensemble $\mathcal{E}$ coincides with supersystem $\mathcal{S}$, then the treatment is self-contradictory because the elementary constituents of $\mathcal{E}$ should be simultaneously distinguishable and

indistinguishable. If, on the contrary, a distinction is made between $\mathcal{E}$ and $\mathcal{S}$, then the treatment proves only that $\$(\rho)$ is $1/N$ times the thermodynamic entropy of $\mathcal{S}$. Indeed, a similar result can be obtained by a simpler treatment, in which a mixture of ideal gases with arbitrary elementary constituents and with molecular fractions given by the eigenvalues of ρ is associated with $\mathcal{E}$, as it is shown in the following.

Let us consider a mixture of orthogonal states $\mathcal{E}\{c_n, |\varphi_n\rangle\}$, with N elements, described by density operator $\rho = \sum_{n=1}^{q} c_n |\varphi_n\rangle\langle\varphi_n|$. Let us associate with $\mathcal{E}\{c_n, |\varphi_n\rangle\}$ a mixture $\mathcal{G}$, with N molecules, of q pure ideal gases $\mathcal{G}^{[1]}, \mathcal{G}^{[2]}, \ldots, \mathcal{G}^{[q]}$ with molecular fractions $c_1, c_2, \ldots, c_q$, in a state $\mathcal{G}_1$ defined as follows. Gases $\mathcal{G}^{[1]}, \mathcal{G}^{[2]}, \ldots, \mathcal{G}^{[q]}$ are mixed, i.e. are not separated by internal walls, and $\mathcal{G}$ is in the stable equilibrium state with temperature T and volume V.

In this correspondence, the distinguishability of two molecules which belong to different gases represents the distinguishability of two different states of the set $\{|\varphi_n\rangle\}$, which has been proved in theorem 1. Moreover, the mixing of gases $\mathcal{G}^{[1]}, \mathcal{G}^{[2]}, \ldots, \mathcal{G}^{[q]}$ represents the lack of knowledge of the quantum mechanical state of each replica of A. Note that, if $\{|\varphi_n\rangle\}$ is not an orthogonal set of states, the states of $\{|\varphi_n\rangle\}$ are not distinguishable on account of theorem 2 and the correspondence between $\mathcal{E}\{c_n, |\varphi_n\rangle\}$ and $\mathcal{G}$ becomes meaningless.

Let us call $\mathcal{G}_2$ the state of $\mathcal{G}$ in which gases $\mathcal{G}^{[1]}, \mathcal{G}^{[2]}, \ldots, \mathcal{G}^{[q]}$ are separated by internal walls and are in the stable equilibrium states with temperature T and volumes $c_1 V, c_2 V, \ldots, c_q V$ respectively. The following theorem holds.

Theorem 3. The entropy difference between states $\mathcal{G}_1$ and $\mathcal{G}_2$ of system $\mathcal{G}$ is given by:

$$S(\mathcal{G}_1) - S(\mathcal{G}_2) = -Nk \operatorname{Tr}(\rho \ln \rho). \tag{3.1}$$

Proof. A well known result of thermodynamics is that the entropy of $\mathcal{G}$ in state $\mathcal{G}_1$ equals the sum of the entropies of gases $\mathcal{G}^{[1]}, \mathcal{G}^{[2]}, \ldots, \mathcal{G}^{[q]}$ when each gas is separated from the others and occupies a volume V at temperature T [7]. Therefore, on account of the additive property of entropy:

$$S(\mathcal{G}_1) - S(\mathcal{G}_2) = \sum_{n=1}^{q} [S(\mathcal{G}_1^{[n]}) - S(\mathcal{G}_2^{[n]})]. \tag{3.2}$$

Since the entropy difference between two neighbouring states of $\mathcal{G}^{[n]}$ with the same temperature is given by $dS = c_n N k dV/V$, eq.(3.2) yields:

$$\begin{aligned} S(\mathcal{G}_1) - S(\mathcal{G}_2) &= \sum_{n=1}^{q} c_n N k \int_{c_n V}^{V} \frac{dV}{V} \\ &= -Nk \sum_{n=1}^{q} c_n \ln c_n = -Nk \, \mathrm{Tr}(\rho \ln \rho). \end{aligned} \tag{3.3}$$

Let us now take $S(\mathcal{G}_2) = 0$. Then, on account of theorem 3:

$$S(\mathcal{G}_1) = -Nk \, \mathrm{Tr}(\rho \ln \rho). \tag{3.4}$$

The condition $S(\mathcal{G}_2) = 0$ can be satisfied, for instance, by taking $S(\mathcal{G}_2^{[n]}) = 0$ for every n. This assumption is legitimate, because only entropy differences are defined in thermodynamics. Furthermore, the entropy difference between two states of a closed system is defined only if these states can be interconnected by a reversible process in which only heat and work interactions between the system and its environment are allowed [8]. Therefore, since no reversible process which involves only heat and work interactions can either transform a state of a pure gas into a state of a different pure gas or create particles, a reference state for each pure gas and each number of particles must be chosen. Moreover, no restriction exists on the entropy value that can be assigned to a system in its arbitrarily chosen reference state.

Definition of mixing entropy. Let us define *mixing entropy of a mixture of orthogonal states* $\mathcal{E}\{c_n, |\varphi_n\rangle\}$ the quantity:

$$\overline{S}(\mathcal{E}\{c_n, |\varphi_n\rangle\}) = \lim_{N \to \infty} \frac{S(\mathcal{G}_1)}{N}, \tag{3.5}$$

where the limit $N \to \infty$ has been introduced because a quantum ensemble has, in principle, infinite elements.

On account of eqs.(3.4) and (3.5):

$$\overline{S}(\mathcal{E}\{c_n, |\varphi_n\rangle\}) = -k \, \mathrm{Tr}(\rho \ln \rho). \tag{3.6}$$

If $\rho = \sum_n |\varphi_n\rangle\langle\varphi_n|$ has infinite nonvanishing eigenvalues, the mixing entropy of $\mathcal{E}\{c_n, |\varphi_n\rangle\}$ can be defined as follows. First, let us consider a density operator $\rho' = \sum_{n=1}^{q} c_n |\varphi_n\rangle\langle\varphi_n|$ and define functional $\overline{S}_q$ by

eq.(3.5); then let us take the limit $q \to \infty$ of $\overline{S}_q$. With this definition, eq.(3.6) still holds. If ρ has a continuous spectrum, the mixing entropy of $\mathcal{E}\{c_n, |\varphi_n\rangle\}$ can be defined in a similar way.

Functionals missing information $I(\mathcal{E}\{c_n, |\varphi_n\rangle\})$ and mixing entropy $\overline{S}(\mathcal{E}\{c_n, |\varphi_n\rangle\})$ are defined on the same domain, namely the set of all mixtures of orthogonal states. Moreover, on account of eqs. (2.7) and (3.6), they coincide if the arbitrary constant α in eq. (2.7) equals Boltzmann constant k. In the following, we will take $\alpha = k$, so that:

$$I(\mathcal{E}\{c_n, |\varphi_n\rangle\}) = \overline{S}(\mathcal{E}\{c_n, |\varphi_n\rangle\}) = -k \operatorname{Tr}(\rho \ln \rho). \tag{3.7}$$

The choice $\alpha = k$ is not a physically meaningful constraint on α, because both the value and the physical dimensions of Boltzmann constant are determined conventionally through the definition of thermodynamic temperature, as it will be proved in the following.

Let R_0 be a reference heat reservoir, and T_0 an arbitrarily chosen positive real number associated with R_0. The *thermodynamic temperature* of any heat reservoir R is defined as follows:

$$T = -T_0 \frac{Q}{Q_0}, \tag{3.8}$$

where Q and Q_0 are the quantities of heat absorbed from R and R_0 respectively in a Carnot cycle of any system A between R and R_0 [9]. The ratio Q/Q_0 is negative and depends only on R and R_0, so that T is a property of R with positive values. The value and the physical dimensions of T are determined by the choice of the arbitrary multiplicative constant T_0. Boltzmann constant is then defined by the equation of state of an ideal gas, $pV = NkT$, i.e.:

$$k = \frac{pV}{NT}. \tag{3.9}$$

Eqs.(3.8) and (3.9) point out that the value and the physical dimensions of k are determined by those of T_0. A clear statement of the arbitrariness of Boltzmann constant can also be found in Refs.[10,11]. From Ref.[10] we quote: "Boltzmann's constant may be regarded as a correction factor necessitated by our custom of measuring temperature in arbitrary units derived from the freezing and boiling points of water. Since the product TS must have the dimensions of energy, the units in which entropy is measured depend on those chosen for temperature".

IV. A disagreement between von Neumann's entropy and the highest entropy principle

In this section we prove that the interpretation of functional $\$(\rho) = -k\,\mathrm{Tr}(\rho \ln \rho)$ as $1/N$ times the entropy of any after-measurement ensemble with N elements is incompatible with the highest entropy principle.

A system $\mathcal{B}$ will be called *environment* of a system $\mathcal{A}$ if $\mathcal{B}$ is the smallest system such that $\mathcal{A}+\mathcal{B}$ is isolated. Let $\mathcal{A}$ be a system and $\mathcal{B}$ its environment. An equilibrium state [12] of $\mathcal{A}$ will be called a *stable equilibrium state* if it is impossible to change it by a process of $\mathcal{A}+\mathcal{B}$ in which $\mathcal{B}$ performs a cycle [12]. A system $\mathcal{N}$ will be called a *normal system* if, starting from any state of $\mathcal{N}$, there exists a weight process [13] of $\mathcal{N}$ in which the energy of $\mathcal{N}$ increases, the external parameters of $\mathcal{N}$ remain unchanged, and $\mathcal{N}$ is brought to a nonequilibrium state. The simplest example of weight process is a process in which the only effect external to the system is the displacement of a pointlike mass in a uniform gravitational field. A stable equilibrium state $\mathcal{A}_s$ of $\mathcal{A}$ will be called *normal* if either $\mathcal{A}$ is normal or there exists a stable equilibrium state $\mathcal{N}_s$ of a normal system $\mathcal{N}$ such that $\{\mathcal{A}_s, \mathcal{N}_s\}$ is a stable equilibrium state of $\mathcal{A}+\mathcal{N}$. A stable equilibrium state which is not normal will be called *special*. A corollary of the definition of normal stable equilibrium state is the *impossibility of a perpetual motion machine of second kind* ($PMM2$), which can be stated as follows.

It is impossible to perform a weight process of a system $\mathcal{A}$ such that: the process starts from a normal stable equilibrium state of $\mathcal{A}$, the work done by $\mathcal{A}$ is positive and the external parameters of $\mathcal{A}$ remain unchanged.

This corollary is proved for instance in Ref.[14]. It represents a generalization of Kelvin-Planck's statement of the second law of thermodynamics.

The *highest entropy principle* can be stated as follows.

Among the states of a system that have a given composition, given external parameters and a given energy value, the highest entropy state is unique and coincides with the unique stable equilibrium state [15].

For a system of N identical spin-1/2 particles in a uniform classical magnetic field $\vec{h}$, the highest entropy principle ensures that for any allowed energy value the highest entropy state is unique and coincides with the unique stable equilibrium state. On the set of stable equilibrium

states of this system, thermodynamic temperature is defined as follows:

$$T = \left(\frac{\partial E}{\partial S}\right)_{N,\vec{h}}. \tag{4.1}$$

The stable equilibrium states with positive temperature are normal, while those with negative temperature are special [16].

Let us consider an ensemble $\mathcal{E}$ of spin-1/2 systems interacting with an external magnetic field $\vec{h}$. The hamiltonian of each system is:

$$H = -\mu\vec{\sigma}\cdot\vec{h}, \tag{4.2}$$

where $\vec{\sigma} = (\sigma_x, \sigma_y, \sigma_z)$, σ_x, σ_y and σ_z are the Pauli matrices, μ is the magnetic coupling constant which will be taken as positive. Let $|E_-\rangle$ and $|E_+\rangle$ be the eigenstates of the hamiltonian which correspond to the energy levels $E_- = -\mu h$ and $E_+ = \mu h$ respectively, where h is the magnetic field intensity.

An ideal measurement of the spin component of each system along the direction of $\vec{h}$ is also an ideal measurement of energy. When such a measurement has been performed, the after-measurement ensemble, $\hat{\mathcal{E}}$, is described by density operator

$$\rho = a|E_-\rangle\langle E_-| + b|E_+\rangle\langle E_+|, \tag{4.3}$$

where a and b are real positive coefficients.

Eq.(4.3) can be rewritten as :

$$\rho = \frac{e^{-\frac{H}{kT}}}{\mathrm{Tr}(e^{-\frac{H}{kT}})}, \tag{4.4}$$

where H is the hamiltonian operator (4.2), k is Boltzmann constant and T is a real number with the physical dimensions of a temperature, determined as follows.

Eq.(4.4) can be written as:

$$\rho = \frac{1}{1+e^{-\frac{2\mu h}{kT}}}|E_-\rangle\langle E_-| + \frac{1}{1+e^{\frac{2\mu h}{kT}}}|E_+\rangle\langle E_+|. \tag{4.5}$$

Eqs.(4.3) and (4.5) agree if:

$$a = \frac{1}{1+e^{-\frac{2\mu h}{kT}}}, \tag{4.6a}$$

$$b = \frac{1}{1 + e^{\frac{2\mu h}{kT}}}. \tag{4.6b}$$

One of the above equations is redundant on account of the normalization condition $1 = \mathrm{Tr}\rho = a + b$. We can solve, for example, eq.(4.6b) and express T as a function of b:

$$T = \frac{2\mu h}{k[\ln(\frac{1}{b} - 1)]}. \tag{4.7}$$

Let us assume, according to von Neumann, that $\hat{\mathcal{E}}$ can be considered as a thermodynamic system with entropy $S = N\$(\rho) = -Nk\ \mathrm{Tr}(\rho \ln \rho)$ and energy $E = N\ \mathrm{Tr}(\rho H)$. As it is well known [17], (4.4) is the unique density operator which maximizes \$ with a constrained value of $\mathrm{Tr}(\rho H)$. Therefore, according to von Neumann's interpretation of functional \$, $\hat{\mathcal{E}}$ is in the highest entropy state for the given values of E, N and h, which, on account of the highest entropy principle, is a stable equilibrium state. The temperature of this state is the real number T given by eq.(4.7), which satisfies the general definition of thermodynamic temperature applied to a system of N spin-1/2 particles in a uniform classical magnetic field, given by eq.(4.1). In fact, from eq.(4.3) one obtains:

$$S = -Nk\ \mathrm{Tr}(\rho \ln \rho) = -Nk[b \ln b + (1 - b) \ln(1 - b)]. \tag{4.8}$$

From eqs.(4.2) and (4.3):

$$E = N\ \mathrm{Tr}(\rho H) = N[aE_- + bE_+] = N\mu h(2b - 1). \tag{4.9}$$

Therefore:

$$\left(\frac{\partial E}{\partial S}\right)_{N,h} = \left(\frac{\partial E}{\partial b}\right)_{N,h} \left(\frac{\partial S}{\partial b}\right)_N^{-1} = \frac{2\mu h}{k[\ln(\frac{1}{b} - 1)]} = T. \tag{4.10}$$

On account of eq.(4.8), S is a monotonic increasing function of b in the range $b \leq 1/2$, it is monotonically decreasing in the range $b \geq 1/2$ and has an absolute maximum, $S_{max} = Nk \ln 2$, when $b = 1/2$. As a consequence of eq.(4.7), if $b < 1/2$ then $T > 0$ and the stable equilibrium states of $\hat{\mathcal{E}}$ are normal; if $b > 1/2$ then $T < 0$ and the stable equilibrium states of $\hat{\mathcal{E}}$ are special.

We have shown that von Neumann's interpretation of functional \$ and the highest entropy principle imply that, if $b < 1/2$, $\hat{\mathcal{E}}$ is a system

in a normal stable equilibrium state. On the contrary, it is possible to absorb energy from the after-measurement ensemble $\hat{\mathcal{E}}$ and perform positive work, with no other effect in the environment of $\hat{\mathcal{E}}$, in contrast with the impossibility of $PMM2$; therefore, $\hat{\mathcal{E}}$ is not in a normal stable equilibrium state.

In fact, $\hat{\mathcal{E}}$ is an ordered ensemble, composed of two pure subensembles, $\hat{\mathcal{E}}_+$ and $\hat{\mathcal{E}}_-$, separated in space. Ensemble $\hat{\mathcal{E}}_-$ can be considered as a system of aN spins in the ground state; ensemble $\hat{\mathcal{E}}_+$ can be considered as a system of bN spins in the maximum energy state for the given value of h, i.e., in the special stable equilibrium state with negatemperature $-1/T = +\infty$. It is well known that it is possible to absorb energy from $\hat{\mathcal{E}}_+$ and perform positive work, with no other effect in the environment of $\hat{\mathcal{E}}_+$ [16].

Our analysis proves that the interpretation of functional $\$(\rho) = -k \operatorname{Tr}(\rho \ln \rho)$ as $1/N$ times the entropy of any after-measurement ensemble with N elements violates the highest entropy principle.

Note that the before-measurement ensemble $\mathcal{E}$ cannot be considered as a thermodynamic system. In fact, if $\mathcal{E}$ were a thermodynamic system it could reach a stable equilibrium state. Then, the measuring apparatus could be considered as a Maxwell demon acting on $\mathcal{E}$, because, starting from a stable equilibrium state of $\mathcal{E}$, it would allow a separation of $\mathcal{E}$ into two sybsystems in non-equilibrium with each other. In this case, the thermodynamic state of the measuring apparatus would remain unchanged. In fact, in a Stern-Gerlach apparatus the magnetostatic field is left unchanged by the interaction with the ensemble of spin-1/2 particles. As it has been pointed out by Szilard [18], a Maxwell demon which does not undergo an entropy increase during the measurement process violates Kelvin-Planck's statement of the second law of thermodynamics.

V . Conclusions

Quantum ensembles have been classified according to information which may be available in addition to the knowledge of density operator ρ. Then, a missing information functional has been defined. Moreover, von Neumann's treatment of functional $\$(\rho) = -k \operatorname{Tr}(\rho \ln \rho)$ has been analysed and restated in order to prove that, for a mixture of orthogonal states described by a density operator ρ, $\$(\rho)$ equals $1/N$ times the entropy of an N-particle mixture of ideal gases associated with the ensemble. Finally, it has been proved that the interpretation of functional

$\$(\rho)$ as $1/N$ times the entropy of any ensemble with N elements and described by ρ is incompatible with the highest entropy principle.

Acknowledgments

The authors are grateful to Prof. S. Bergia for helpful discussions on the topics of this paper. Financial support has been provided by Ministero dell'Università e della Ricerca Scientifica e Tecnologica.

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(Manuscrit reçu le 5 novembre 1993)